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Registry No. 1 (copolymer), 121753-88-6; **1b** (copolymer), 126724-55-8; 2 (copolymer), 126724-56-9; 7 (copolymer), 126724-57-0; 8 (copolymer), 126724-58-1; 9 (copolymer), 126724-59-2; iodine, 7553-56-2.

Synthesis, Electrochemical Characterization, and Assembly into Langmuir–Blodgett Films of Some N-Substituted Derivatives of Poly(3,6-carbazolylmethylene)

Stephen V. Lowen,* John Buschek, R. Mastantuono, and David A. Holden†

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

G. J. Kovacs and R. O. Loutfy

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1

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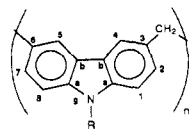
ABSTRACT: A series of condensation polymers of N-substituted carbazoles with formaldehyde were prepared by H_2SO_4-catalyzed oligomerization in dioxane. Soluble polymers having number-average degrees of polymerization of 5–30 were obtained and characterized spectroscopically. These polymers underwent irreversible one-electron oxidation in CH_2Cl_2 solution with electrodeposition and displayed intense blue and green electrochromism. Homopolymers and copolymers in which the 9-position of the carbazole ring was substituted by flexible polar groups such as $(CH_2)_4CN$, $(CH_2)_{10}COOH$, or $(CH_2)_{11}OH$ spread reproducibly from $CHCl_3$ to give monolayers at the air–water interface. Mixed monolayers containing as little as 0.25 mol of stearic acid/1 mol of repeating unit gave Y-deposition on quartz, with the formation of LB films of up to 70 monolayers in thickness.

Introduction

Monolayers at the air–water interface, which have sufficiently high collapse pressures, can be transferred as Langmuir–Blodgett (LB) films to a variety of solid substrates and then used in further applications. Interest in LB films has recently undergone a period of dramatic growth, particularly as a result of their potential applications as components of microelectronic devices, as high-resolution photoresists for microlithography, and as nonlinear optical components.[1–7] A major trend in LB film research is to move from simple saturated fatty acids, which function as insulating layers, to functional surface-active compounds, which are electrochemically or photochemically active. In addition, polymeric LB films offer the important advantage of higher mechanical stability than small-molecule films.[5–9]

In this paper we report the synthesis and characterization of stable, transferable surface-active polymers that incorporate a redox-active aromatic amine group in the backbone. Homopolymers and copolymers based on derivatives of poly(3,6-carbazolylmethylene) with the general structure



1a, R = $(CH_2)_4CN$
1b, R = $(CH_2)_{10}COOH$
1c, R = $(CH_2)_{11}OH$
1d, R = $(CH_2)_{13}CH_3$

were investigated. These polymers contain nitrile, carboxylic acid, and alcohol polar groups, which result in enhanced stability of monolayers at the air–water interface. The spreading behavior of these polymeric monolayers and of mixed monolayers with stearic acid was

† Deceased.

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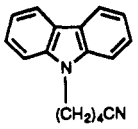
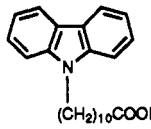
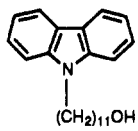
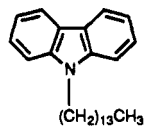
Table I
Physical and Spectral Constants for N-Substituted Carbazole Monomers

monomer	name	MP, °C	IR (ν), cm^{-1}	^{1}H NMR, δ
	1a	123	3049 (arom, = CH) 2939, 2879 (CH) 2244 (CN) 1623, 1591 (arom)	7.0–8.1 (m, 8 H, arom) 4.15 (t, 2 H, ArCH) 1.2–2.1 (m, 6 H, CH)
	1b	95	3049 (arom, =CH) 2925, 2850 (CH) 1705 (C=O) 1625, 1595 (arom) 1410 1237 (CO)	10.9 (s, br, 1 H, COOH) 7.1–8.2 (m, 8 H, arom) 4.3 (t, 2 H, ArCH) 2.35 (t, 2 H, CHCOO) 1.2–2.0 (m, 16 H, CH)
	1c	74–75	3328 (OH) 3047 (arom, =CH) 2920, 2850 (CH) 1625, 1595 (arom)	7.2–8.2 (m, 8 H, arom) 4.3 (t, 2 H, ArCH) 3.6 (t, 2 H, *CH*OH) 1.2–2.0 (m, 18 H, CH)
	1d	41–42	3045 (arom, =CH) 2915, 2845 (CH) 1625, 1596 (arom)	7.0–8.1 (m, 8 H, arom) 4.2 (t, 2 H, ArCH) 0.7–2.0 (m, 27 H, CH)

investigated using Langmuir balance techniques. In addition, the electrochemical properties of these polymers were studied utilizing stationary voltammetric techniques. The goal of this research is to create redox-active and electrochromic polymers that form sufficiently stable monolayers to permit assembly into multilayers on solid supports by the Langmuir–Blodgett method.

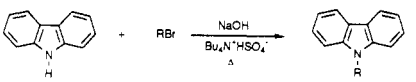
Redox-active aromatic amine groups such as carbazole are interesting for several reasons. They possess intense UV absorption spectra and have been used extensively as donors in studies of photoinduced energy transfer and electron transfer to acceptor molecules.[10,11] Additionally, their redox properties have been investigated and utilized in electrochemical systems,[12] as well as in studies of electron donor–acceptor complexation.[13-16] The combination of these properties makes carbazole-containing polymers attractive for potential LB applications such as charge-rectifying hole-transporting layers in xerographic devices or as electrochromic materials in fast-display or data-reading devices.

Experimental Details

Materials. Water was purified to a resistivity at 18 MΩ·cm through a pair of Milli-Q filtration systems operating in series. All other solvents were HPLC grade and used without further purification. Tetrabutylammonium tetrafluoroborate (TBABF$_4$; Aldrich) and tetrabutylammonium perchlorate (TBAP; Aldrich) were dried for several hours in vacuo. All other reagents were used as received.

Techniques. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-250 and AC-300 instruments. UV/visible spectra were recorded on a Cary 118 spectrometer. Monolayer measurements were made on a Langmuir balance, and surface pressures were determined using a Wilhelmy plate consisting of a 1.0 × 1.0 cm square of filter paper. A Hewlett-Packard Model 3421A data acquisition unit and a Hewlett-Packard 87 XM computer were utilized for apparatus control, data logging, and plotting. A Lauda Model FL-1 film lift was used for the monolayer transfer experiments. For cyclic voltammetry measurements a 25-mL two-compartment cell with a 2.6-mm^2 Pt disk working electrode, a Pt foil counter electrode, and a saturated calomel reference electrode (SCE) were used. The electrochemical instrumentation consisted of an EG&G PAR Model 174A polarographic analyzer with a Model 175 universal programmer. The cell was bubbled with argon prior to the experiment and kept under an inert atmosphere. Number-average molecular weight measurements were performed on a Corona Wescan vapor pressure osmometer using 1,2-dichloroethane as the solvent.

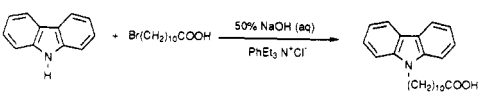
Synthesis of Monomers. All monomers with the exception of the acid-substituted derivative were synthesized by a modification of the procedure outlined by Rodriguez-Parada and Percec[13] and shown in the following equation:



(1)

In a typical experiment, 0.030 mol of carbazole (Baker), 0.045 mol of the ω-bromo hydrocarbon, 0.045 mol of powdered NaOH, and 0.94 mmol of tetrabutylammonium hydrogen sulfate were mixed in 25 mL of acetone. This was heated to reflux with stirring for at least 3 h. The product was precipitated into 400 mL of ice water, collected by suction filtration, and recrystallized several times from isopropyl alcohol. The yields were about 50%, and TLC tests showed no residual starting material. Infrared spectra showed no evidence of an N–H band corresponding to unreacted carbazole.

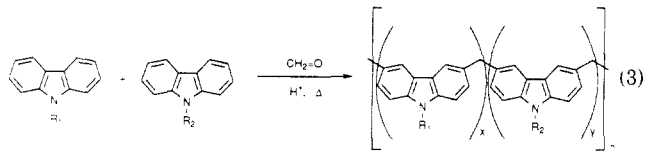
The synthesis of **1b** was based on a procedure outlined by Hsieh and Litt[17] and shown in the following scheme:



(2)

In a typical reaction 1.50 × 10^{-2} mol of carbazole, 2.07 × 10^{-2} mol of *n*-bromoundecanoic acid (Aldrich), 4.4 × 10^{-4} mol of benzyltriethylammonium sulfate, and 10 mL of 50% aqueous NaOH were added to 50 mL of either benzene or 1,4-dioxane. This was allowed to react with stirring overnight. The mixture was poured into 400 mL of dilute HCl and then extracted with diethyl ether. The solvent was evaporated to yield a white product, which was recrystallized several times from isopropyl alcohol. The final yield was 49%, and TLC and IR spectroscopy showed no residual carbazole. The physical and spectral constants of each monomer are summarized in Table I.

Preparation of Carbazolylmethylene Condensation Polymers. An acid-catalyzed condensation polymerization with formaldehyde, originally reported by Bruck,[18] was utilized for all polymer synthesis (eq 3). In a typical reaction, 2.7 × 10^{-3} mol of paraformaldehyde and 2 drops of concentrated H_2SO_4 were added to 1.65 × 10^{-3} mol of monomer (or a total of 1.65 × 10^{-3} mol of comonomers) in 7 mL of 1,4-dioxane. The reaction


(3)

was kept under N_2 and heated at 85 °C for 2–3 h. The resultant blue solution was poured into 400 mL of methanol, and a blue-green precipitate was collected by suction filtration. After several washings with fresh methanol, the polymer was allowed to dry in air. The yields ranged from 31 to 87%, and typical spectral results and elemental analyses are listed in Table II. In experiments to establish that the methanol-extracted polymers were free of unreacted N-substituted carbazole monomer, the polymers were also extracted several times with boiling isopropyl alcohol.

Determination of Copolymer Composition. Several approaches to the determination of copolymer composition were compared. Copolymer compositions were calculated from C, H, or alternatively N elemental analyses assuming no end groups, hydrolysis, or cross-linking. There are two difficulties associated with this method: the precision is low, corresponding in some cases to ±20% in the mole fractions, and the nitrogen analyses for some of the polymers lie outside the expected ranges. Reasons for high N analyses may include incomplete combustion, excess N-substituted carbazole end groups, or the formation of branches. A more satisfactory method of determination of composition was from ^{1}H NMR spectra acquired with relaxation delays of 5 s or more. From the relative integration signals of the $ArCH_2Ar$ and NCH_2 signals at δ 3.8–4.4 and other well-resolved signals in the spectrum, copolymer compositions were calculated with an estimated accuracy of ±10% of the stated mole fractions. Suitable resonances included the CH_2OH signal at δ 3.5 for copolymers of **1c** or the CH_2COOH signal at δ 2.3 for copolymers of **1b**. For the poly(**1a**-*co*-**1d**) series the entire alkyl group signal between δ 2.0 and 0.8 was used to determine composition. A further check of composition was provided by the relative areas of selected alkyl resonances in ^{13}C NMR spectra acquired with relaxation delays of 20 s. For example, the $CH_2CH_2C{\equiv}N$ resonance at δ 23.2 and the CH_2CH_3 resonance at δ 22.8 were used to verify copolymer compositions in the poly(**1a**-*co*-**1d**) series.

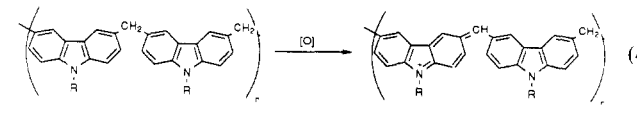
Results and Discussion

Polymer Synthesis and Structural Characterization. The carbazole–formaldehyde condensation polymers prepared in this study were generally blue-green powders soluble in methylene chloride, 1,2-dichloroethane, and chloroform. The structures of the polymers were established by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Particularly useful in structure elucidation was the availability of numerous small-molecule 3- and 3,6-substituted *N*-alkylcarbazoles in our laboratory as the result of a separate project.[19] Our assignments of the ^{13}C resonances of the polymers are in agreement with those of Watarai,[20] with the exception that at spectrometer frequencies of 63.0 and 75.4 MHz the six aromatic C resonances of the copolymers and low molecular weight homopolymers are no longer single lines. We attribute the splittings to sequence and end-group effects in relatively short polymer chains and not to weak shielding effects by adjacent carbazole rings.[20] On alkyl substitution or condensation polymerization with formaldehyde the ^{13}C resonances of the C-3 and C-6 carbazole ring carbons shift from δ 119 to 132–133 and are clearly recognized as quaternary carbons by a DEPT pulse experiment. The 3,6-methylene link in the polymers is observed by ^{13}C NMR spectroscopy at δ 42 from TMS. This means that in some polymers such as poly(**1a**) it overlaps the signal of the C-1 methylene of the *N*-alkyl chain, which occurs at δ 41.8. In other samples, such as poly(**1d**), the NCH_2 signal is shifted to δ 43.3 and the two resonances are well separated. No evidence was found by ^{13}C NMR spectroscopy for the formation of $-CH_2O-$ linkages, which give rise to resonances in the δ 60–70 range. If the polymerization is interrupted at low conversion, then the terminal $ArCH_2OH$ group is observed as a ^{13}C resonance at δ 67.9. The corresponding signal in the ^{1}H NMR spectrum is a broad singlet or poorly resolved triplet at δ 4.65. Evidence for the existence of *N*-alkylcarbazolyl end groups is provided by weak ^{13}C resonances at δ 140.7, 125.4, and 118.5. These are assigned to carbons at positions a, 4, and 2 of the monosubstituted carbazole ring system, respectively, by comparison with the spectra of 3-(*N*-tetradecylcarbazolyl)methanol and *N*-tetradecylcarbazole. Molecular weights calculated from the relative intensities of these end-group resonances are in agreement with the results of molecular weight determinations by vapor-phase osmometry.

The ^{1}H NMR spectra of the polymer samples display the broad bands typical of high molecular weight materials. Table II summarizes band positions for several samples. The signals from the bridging CH_2 and the $N-CH_2$ group overlap in the range δ 3.8–4.4. The breadth of the signals limits the use of ^{1}H NMR spectroscopy as a structural tool for these polymers. The spectra are useful, however, in establishing the absence of *N*-alkylcarbazole monomers in the polymers following precipitation and washing with methanol.

Table II lists the positions of important bands in the IR spectra of the polymers. The polymers also showed a moderately strong band at 800 cm^{-1}, assigned to the C–H bending mode of the 1,2,4-trisubstituted benzene ring of the carbazole groups in the polymer. IR spectra also showed that the functional groups in the *N*-alkyl chains of the carbazole monomers survived the polymerization conditions, with one exception. During the acid-catalyzed condensation reaction the nitrile group in poly(**1a**) and related copolymers underwent partial (<20%) hydrolysis to a primary amide, which was identified from its IR carbonyl band at 1660 cm^{-1}, as well as a C=O band in the ^{13}C NMR spectrum at δ 172.0. Thus the surface activity of poly(**1a**) and copolymers corresponds to a material with two hydrophilic groups, the unreacted nitrile group and the amide hydrolysis product.

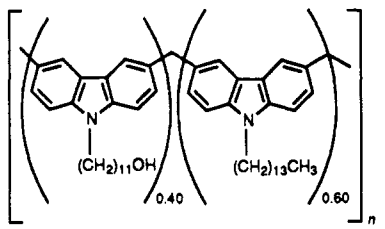
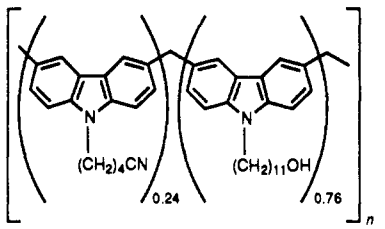
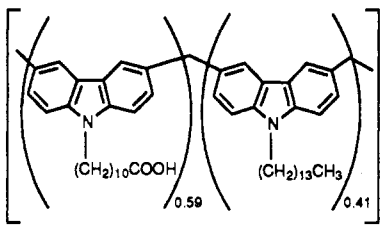
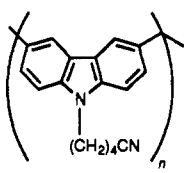
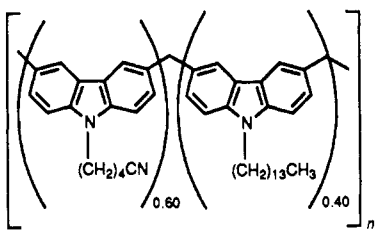
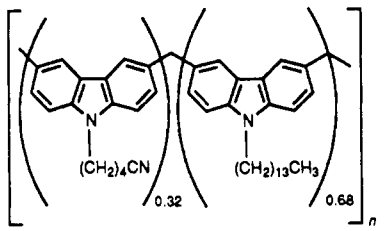
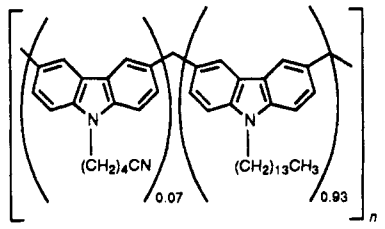
The UV/visible spectrum of poly(**1a**-*co*-**1c**) shown in Figure 1 demonstrates characteristic carbazole absorptions at approximately 240, 270, 296, 335, and 350 nm. In addition, a broad band was observed in the visible region at 590–620 nm. This corresponds to a model compound absorption observed by Bruck et al.[21] for the cation of the dimer bis(9-ethyl-3-carbazolyl)methane. Thus, the polymer autoxidizes partially, as in the following equation:


(4)

When Bruck's value of 6.4×10^4 M^{-1} cm^{-1} for the extinction coefficient of the cation dimer at 630 nm is used, the extents of oxidation of the polymers were calculated to be between 0.08% and 0.2%. These low values are also reflected in the ^{1}H NMR results, where no evidence of an unsaturated methine linkage was observed.

The number-average molecular weights determined by vapor-pressure osmometry ranged between 1300 and 9500, and the corresponding degrees of polymerization were 5–30 units. These values are in agreement with those

Table II
Physical and Spectral Constants for 3,6-Carbazolylmethylene Polymers 1a–1d

polymer[a]	name	elem anal. C	H	N	IR (ν), cm^{-1}	^{1}H NMR, δ
	poly(**1c**-*co*-**1d**)	83.88	9.38	5.73	3361 (OH) 3050 (=CH, arom) 2922, 2850 (CH) 1624, 1581 (arom) 1243 (CO)	7.2–8.2 (br, arom) 4.0–4.4 (br, $ArCH_2$ and $ArCH_2Ar$) 0.9–2.0 (br, alkyl CH)
	poly(**1a**-*co*-**1c**)	82.77	7.94	6.74	3394 (OH) 3006 (=CH, arom) 2921, 2847 (CH) 2243 (CN) 1623, 1599 (arom) 1229 (CO)	7.0–8.1 (br, arom) 3.5–4.5 (br, $ArCH_2$ and $ArCH_2Ar$) 1.0–2.2 (br, alkyl CH)
	poly(**1b**-*co*-**1d**)	81.47	8.76	3.50	3013 (=CH, arom) 2923, 2851 (CH) 1708 (C=O) 1629, 1606 (arom)	7.0–8.2 (br, arom) 3.9–4.6 (br, $ArCH_2$ and $ArCH_2Ar$) 0.8–2.5 (br, alkyl CH)
	poly(**1a**)	80.91	6.26	12.16	3008 (=CH, arom) 2929 (CH) 2241 (CN) 1658 (C=O) 1597 (arom)	6.8–8.2 (m, br, arom) 4.2 (s, br $ArCH_2Ar$) 4.0 (s, br, $ArCH_2$) 1.1–2.3 (m, br, alkyl CH)
	poly(**1a**-*co*-0.40 **1d**)[b]	82.49	7.57	9.61	3049, 3015 (=CH, arom) 2924, 2851 (CH) 2245 (CN) 1667 (C=O)	6.8–8.2 (br, arom) 3.6–4.4 (br, $ArCH_2$ and $ArCH_2Ar$) 0.7–2.3 (br, alkyl CH)
	poly(**1a**-*co*-0.68 **1d**)[b]	85.29	7.94	5.54	3046, 3013 (=CH, arom) 2918, 2851 (CH) 2244 (CN) 1623, 1601 (arom)	6.8–8.2 (br, arom) 3.8–4.4 (br, $ArCH_2$ and $ArCH_2Ar$) 0.7–2.3 (br, alkyl CH)
	poly(**1a**-*co*-0.93 **1d**)[b,c]	86.61	9.86	4.50	3007 (=CH, arom) 2916, 2846 (CH) 2242 (CN) 1623, 1606 (arom)	7.0–8.2 (br, arom) 4.0–4.4 (br, $ArCH_2$ and $ArCH_2Ar$) 0.8–2.1 (br, alkyl CH)

[a] Copolymer compositions were determined by ^{1}H NMR spectroscopy. [b] Poly(**1a**-*co*-0.40 **1d**), poly(**1a**-*co*-0.68 **1d**), and poly(**1a**-*co*-0.3 **1d**) were synthesized using ratios of 10:1, 1:1, and 1:10 nitrile/alkyl monomer in feed, respectively. [c] Copolymer composition was determined by elemental analysis; copolymer structures are idealized structures assuming infinite chain lengths, without cross-linking or end groups.

found previously for poly(*N*-methylcarbazolylmethylene).[16] In general, the molecular weights of polymers formed by a condensation mechanism increase sharply at high monomer conversions. Consequently, our polymerizations were

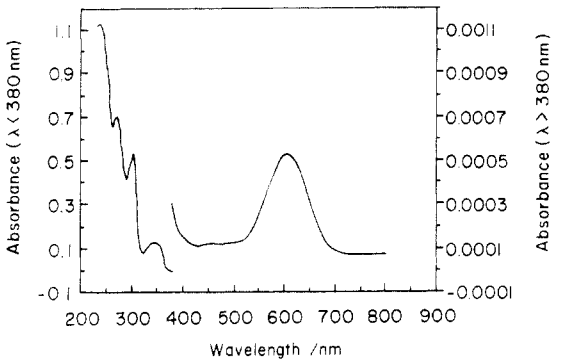


Figure 1. UV/visible spectrum of 3.124×10^{-3} g L^{-1} of poly(**1a**-*co*-**1c**) in $CHCl_3$.

terminated at intermediate conversions to avoid interference from gel formation by cross-linking reactions.

Some degree of cross-linking was evident even at low conversion during the synthesis. A blue-green gel resulted when the polymerization was allowed to proceed to high conversions. Even when the reaction was terminated early enough to collect a soluble blue powder, often the powder became insoluble within a few hours. This is likely due to a combination of cross-linking by continued reaction of CH_2OH end groups, as well as oxidative coupling reactions. Homopolymers or copolymers with high fractions of polar substituents demonstrated the greatest tendency to cross-link; copolymers that contained high fractions of the tetradecyl substituent showed less cross-linking and higher solubility.

Evidence for polar head-group involvement in the cross-linking reactions is seen in a comparison of the IR spectra of a film of poly(**1c**-*co*-**1d**) and a film of the polymer after further reaction with H_2CO, in the presence of H^+ and heat. On treatment of the sample in this manner, a decrease is observed in the relative peak heights of the O-H stretch at 3340 cm^{-1}, the aromatic =CH stretch at 3050 cm^{-1}, and the aromatic C-H out-of-plane deformation at 700–800 cm^{-1}. In addition, a new peak appears at 1520 cm^{-1} corresponding to the C=C stretch in a highly substituted aromatic ring. The data suggest that a polar head group on a neighboring chain reacts with the aromatic ring and subsequently forms a bond. The lower reactivity of the 1 and 8 positions on 3,6,9-trisubstituted carbazole derivatives has been described previously,[22] and it is likely that these are the locations of the cross-links in the polymers as well.

Determination of Copolymer Composition. As a comparison of different methods for measuring copolymer composition, the results for poly(**1a**-*co*-**1d**) prepared from a 1:1 molar mixture of the two carbazole monomers are instructive. The composition was 0.26:0.74 **1a**/**1d** from an average of the C, H, and N elemental analyses, 0.32:0.68 **1a**/**1d** by ^1H NMR spectroscopy, and 0.27:0.73 **1a**/**1d** by ^{13}C NMR spectroscopy. The copolymer syntheses generally yielded copolymer compositions corresponding to the comonomer feed ratios, with the exception of copolymers containing the nitrile comonomer **1a**. In this case, the copolymers had fewer **1a** groups than expected. This is best illustrated by a comparison of poly(**1a**-*co*-0.40 **1d**), poly(**1a**-*co*-0.68 **1d**), and poly(**1a**-*co*-0.93 **1d**) as listed in Table II. In these samples, the monomer feed ratio was varied between 10:1, 1:1, and 1:10 mol of **1a**/**1d**, and in each case, the copolymer contained less **1a** and more **1d** than expected from the feed ratios.

Electrochemical Characterization. The cyclic voltammogram of the hydroxyl monomer **1c** is shown in Figure 2. The peak potential for monomer oxidation occurs

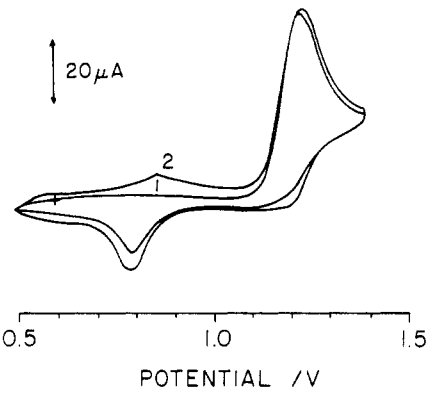


Figure 2. First and second voltammetric scans of 1.0 mM **1a** in 0.10 M TBAP/CH_2Cl_2. Scan rate = 50 mV s^{-1}, potentials measured vs SCE.

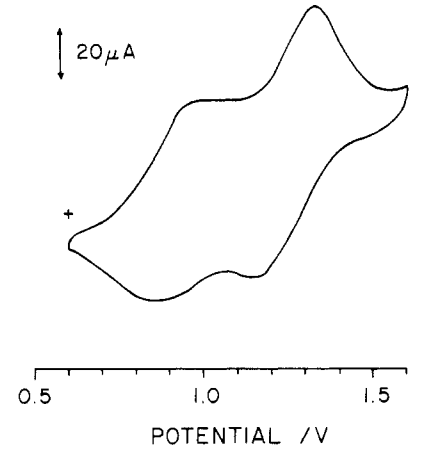


Figure 3. Cyclic voltammogram of 0.992 g L^{-1} of poly(**1c**-*co*-**1d**) (2.73 mM based on the number of carbazole units) in 0.10 M TBAP/CH_2Cl_2. Scan rate = 50 mV s^{-1}, potentials measured vs SCE.

at 1.23 V vs SCE, where the monomeric radical cation species is formed. This oxidation is irreversible as evidenced by the lack of a reverse reduction peak. However, a reduction peak occurs at 0.82 V and, on the second scan, a new oxidation peak occurs at 0.88 V. Similar results have been observed for *N*-alkylcarbazoles,[22] and it was concluded that the radical cation species dimerizes to form a 3,6-bicarbazolyl derivative and that this dimer oxidizes at the lower potential. The reversibility of the dimer oxidation is due to the stabilization of the radical cation by the extended conjugation. The other monomers used in our study showed similar features.

The voltammogram of poly(**1c**-*co*-**1d**) is shown in Figure 3. A broadening of peaks appears, probably due to the extended conjugation of the polymer. The polymer begins to oxidize at about 0.7 V vs SCE, and two irreversible peaks appear after this. The irreversibility can be due to the loss of a hydride ion on the bridging methylene following oxidation or to cross-linking reactions of the reactive radical-cation species. However the nature of the subsequent reactions cannot be conclusively proven from these experiments.

Some of the polymers undergo electrodeposition on the platinum electrode after oxidation. Successive voltammograms of the nitrile polymer poly(**1a**) are shown in Figure 4. The increase in the current magnitude with each scan is indicative of a growing electroactive film on the electrode surface. After several scans, the electrode was removed from solution and a bright blue film was observed on the surface. The voltammogram of the coated electrode in a solution containing only supporting elec-

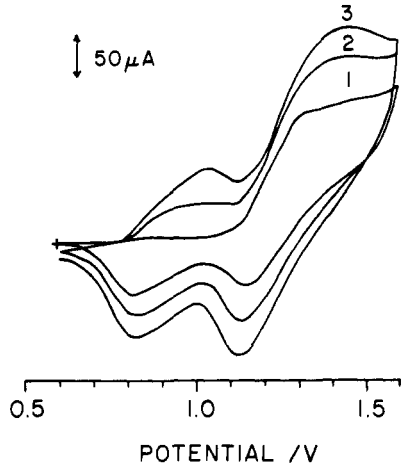


Figure 4. First, second, and third voltammograms of 4.08 g L^{-1} of poly(**1a**) (15.67 mM based on the number of carbazole units) in 0.10 M $TBABF_4/CH_2Cl_2$. Scan rate = 50 mV s^{-1}, potentials measured vs SCE.

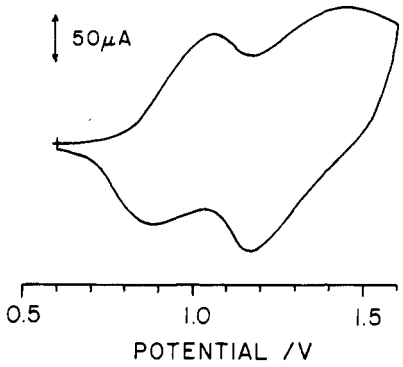


Figure 5. Voltammogram of electrodeposited poly(**1a**) in 0.10 M $TBABF_4/CH_2Cl_2$. Potentials measured vs SCE.

Table III
Summary of the Voltammetric Peak Potentials for Carbazole Monomers and Polymers 1a–1d

compd	$E_{p,ox}$, V	dimerized and/or cross-linked products $E_{p,ox}$, V	$E_{p,red}$, V
1a	1.39	1.05	
1c	1.23	0.87	
1d	1.27	0.91	
poly(**1a**)	1.46	1.06	−0.13
poly(**1a**-*co*-0.68 **1d**)	1.36	0.91	−0.13
poly(**1c**-*co*-**1d**)	1.31	0.95	−0.16

trolyte demonstrates nearly identical features to the solution voltammogram (see Figure 5). The electrode was cycled several times, and a gradual decay of the voltammetric features was observed. A reductive scan to −1.2 V vs SCE showed a small peak at −0.13 V, and the film was observed to turn colorless at this point. After cycling back to 1.1 V, the film appeared green, at 1.4 V the film was a darker green, and after reversing the scan back to 0.6 V it changed back to blue. The characterization of the electrodeposition and the electrochromic properties of these new polymers are being further investigated.

The electrochemical data for all the monomers and the polymers are summarized in Table III. Each polymer generally has similar voltammetric features; any difference in the oxidation peak potentials may be due to the interaction of the polar head group with the carbazole ring in the cross-linking reactions.

Spreading Behavior in Monolayers. Of the monomers prepared in this study only the carboxylic acid **1b** and the alcohol **1c** gave stable monolayers on pure water.

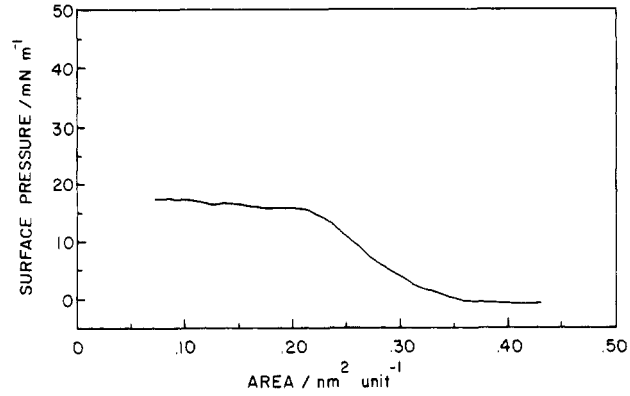


Figure 6. Surface pressure–area isotherm of poly(**1a**-*co*-0.68 **1d**) on pure water subphase at 21 °C.

Table IV
Summary of the Spreading Behavior of Carbazole–Formaldehyde Condensation Polymers

polymer	limiting area, nm^2/repeating unit	collapse pressure, mN/m
poly(**1c**-*co*-**1d**)	0.31	7.0
poly(**1a**-*co*-**1c**)	0.27	14.5
poly(**1b**-*co*-**1d**)	0.32	14.0
poly(**1a**)	0.21	19.0
poly(**1a**-*co*-0.40 **1d**)	0.29	22.0
poly(**1a**-*co*-0.68 **1d**)	0.35	16.0
poly(**1a**-*co*-0.93 **1d**)	not surface active	0

This is in reasonable agreement with the results of Tamai et al.,[10] who found that monolayers of 11-(9-carbazolyl)-undecanoic acid (**1b**) gave expanded phases with low collapse pressures of less than 10 mN m^{-1}.

In contrast to the monomers, many of the homopolymers and copolymers were surface active. In Figure 6, the surface pressure–area isotherm is shown for poly(**1a**-*co*-0.68 **1d**). At about 0.35 nm^2 per repeating unit the surface pressure begins to increase. This is the approximate area required for orientation of the individual carbazole units normal to the plane of the subphase. On further compression, the surface pressure rises until an apparent collapse point is reached at approximately 0.24 nm^2/residue, with a surface pressure of 17 mN m^{-1}. Table IV summarizes the results of the spreading behavior of the other polymers. They show collapse pressures of 10–22 mN m^{-1}, but their molecular areas corresponding to the onset on a condensed phase varied from about 0.20 to 0.35 nm^2/residue. These values are smaller than the footprint of the carbazole repeating unit and suggest substantial imperfection in the spread films. It is likely that the polymer lies on the subphase surface in an irregular coil conformation, with some of the groups oriented normal to the water phase and others simply in a random orientation in the air. The compression area then is not a function of the individual units in the chain but rather a function of the dimensions of the polymer coil. Thus the areas of the condensed phases reflect the extent of crisscrossing of repeating units with the projection of the three-dimensional coil on the surface, as well as the area of the repeating unit.

The presence or absence of polar head groups on the polymer is reflected in the monolayer stability. For instance, the poly(**1a**-*co*-0.93 **1d**) sample, with a high percentage of alkyl substituents, showed no surface activity while polymers with only polar substituents such as pure poly(**1a**) or poly(**1a**-*co*-**1c**) showed the highest collapse pressures. It appears that the best balance between solubility in organic solvents and surface activity at the air–water boundary is attained with polymers containing

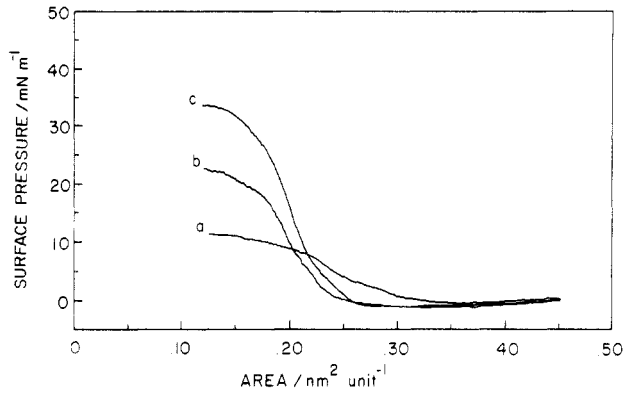


Figure 7. Surface pressure–area isotherms of mixed monolayers of poly(**1c**-*co*-**1d**) and stearic acid on pure water at 21 °C: (a) 0 mol %; (b) 10 mol %; (c) 20 mol % stearic acid.

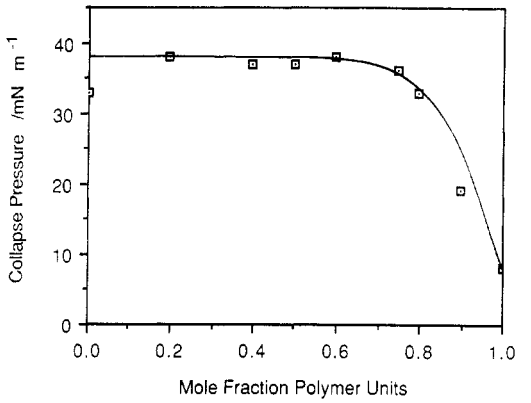


Figure 8. Collapse pressures of monolayers on pure water as a function of molar ratios of poly(**1c**-*co*-**1d**):stearic acid.

approximately 1:1 ratios of polar group substituents to alkyl group substituents.

While many of the polymers indeed give stable monolayers, their collapse pressures are slightly lower than is necessary to achieve transfer to a solid substrate. It has been previously shown than mixtures with long-chain fatty acids result in more stable monolayers.[10] In our work, it was hoped that the addition of a small amount of stearic acid would increase the collapse pressure without significantly affecting the redox behavior of the polymer. This is indeed the case. The π vs A isotherms in Figure 7 demonstrate that the addition of 10–20 mol % stearic acid/1 mol of repeating unit of poly(**1c**-*co*-**1d**) increases the collapse pressures to values well above the required 20 mN m^{-1}. Figure 8 shows results for various mole ratios of polymer to stearic acid. The collapse pressures are relatively constant from 0 to 80 mol % of repeating units and then decrease sharply to the pure polymer value.

If a true random mixture of polymer and stearic acid is achieved, the limiting areas at a chosen pressure should show a linear relationship with the molar composition in the mixture. An example of this additivity behavior is shown in Figure 9, but since the limiting areas of pure stearic acid and pure polymer are similar, no conclusions can be drawn based on this relationship alone. However, when coupled with the observation that the collapse pressures of the mixed monolayers are very different from that of the homopolymer, the data suggest that the stearic acid is randomly dispersed in the polymer matrix on the two-dimensional scale rather than being clustered in individual islands of acid and polymer.[23]

A transfer to a quartz substrate was attempted with monolayers of 80% poly(**1a**-*co*-0.68 **1d**) to 20% stearic acid and of 80% poly(**1b**-*co*-**1d**) to 20% stearic acid. The

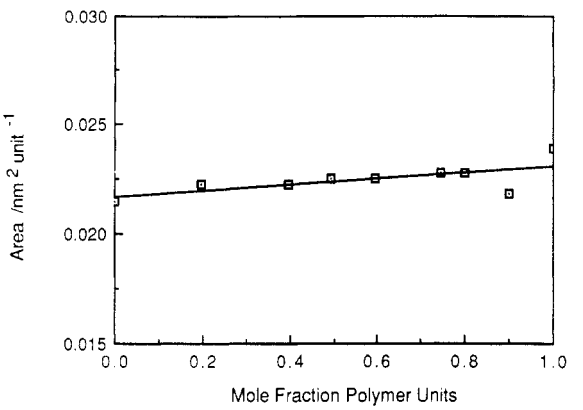


Figure 9. Variation of molecular areas at a constant surface pressure of 10 mN m^{-1} with composition of mixed monolayers of poly(**1c**-*co*-**1d**) and stearic acid.

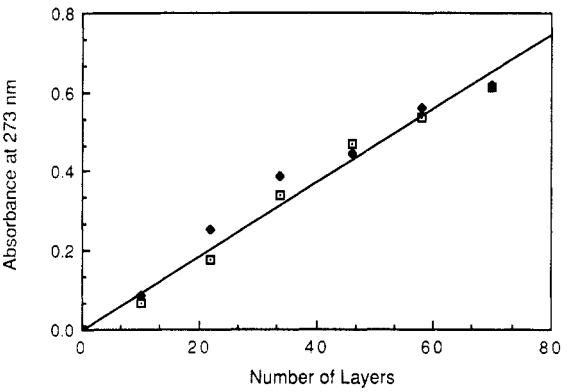


Figure 10. Variation of optical density of LB multilayers during deposition on a quartz disk: (□) 80:20 poly(**1a**-*co*-0.68 **1d**)/stearic acid; (♦) 80:20 poly(**1b**-*co*-**1d**)/stearic acid.

presence of the transferred polymer was monitored by UV spectroscopy at 273 nm, a peak characteristic of the carbazole group. The absorbance of the deposited polymer was measured after every 3 dips of the quartz disk into the monolayer-coated subphase held at a constant pressure of 22 mN m^{-1}. Figure 10 shows that consistent and identical linear deposition ratios occur for these samples up to 70 layers. The movement of the barrier on the Langmuir trough indicated a Y-type deposition; i.e., no compression occurred in the first insertion but compression always occurred thereafter during repeated withdrawal and insertion steps. A full UV spectrum of the coated substrate showed identical band positions to those of the polymer in CH_2Cl_2 solution. These experiments show that consistent transfer to a solid substrate is achievable with mixed monolayers of the carbazole condensation polymers and small amounts of a long-chain fatty acid.

A similar series of experiments were performed on mixed monolayers of stearic acid and poly(**1b**-*co*-**1d**) on a water subphase containing 1.0×10^{-3} M Cd^{2+}. It is well-known that the presence of divalent cadmium ions causes two adjacent carboxylic acid head groups to bind together to one Cd^{2+}, resulting in more compressible monolayers with higher collapse pressures. Figure 11 shows that the collapse pressures of the mixed monolayers are indeed greater for the Cd^{2+} subphase than for the pure H_2O subphase, but the collapse pressure for the pure polymer unmixed with stearic acid is identical in both phases. This indicates that the Cd^{2+} has no effect on the –COOH head groups on the polymer. This is likely because the polar groups in the polymer are constrained by the spacing of the repeating unit and are unable to pack tightly as in

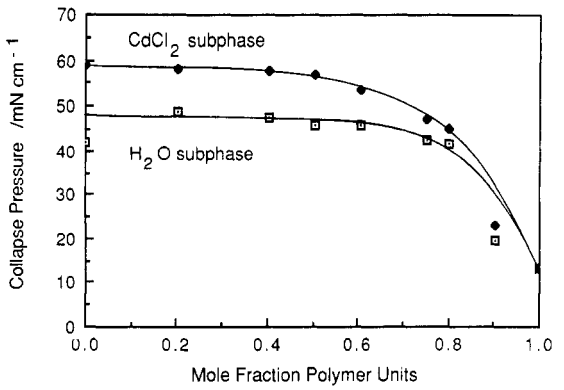


Figure 11. Variation of collapse pressures of mixed monolayers of poly(**1b**-*co*-**1d**) and stearic acid on a water subphase and a 1.0 mM $CdCl_2$ subphase with film composition.

the case of stearic acid.

Transfer to quartz substrates was achieved with a monolayer of 80% poly(**1b**-*co*-**1c**) to 20% stearic acid from the Cd^{2+} subphase at 22 mN m^{-1}. The multilayer deposition was identical with that found for the polymer on the pure water subphase as shown in Figure 11, and this indicates that the polymer is not transferred in a more highly compressed state from $CdCl_2$ solutions. However, since this monolayer mixture has a higher apparent collapse pressure on the Cd^{2+} subphase, it is possible to transfer the film at higher surface pressures than would be possible from a pure water subphase. These results indicate the possibility of transferring highly compressed polymeric multilayers to solid substrates.

Conclusions

Derivatives of poly(3,6-carbazolylmethylene) with polar substituents have been shown to be electrochemically active as well as surface active at the air–water interface. An electrodeposition of the polymers resulted in the formation of redox-active, electrochromic coatings. Highly stable and transferable monolayers were obtained from mixtures of these carbazole polymers with stearic acid. The combination of redox activity and electrochromism in a stable LB film suggests that these polymers may have interesting applications in new types of displays and electroimaging devices. We are currently investigating the electrochemical and spectroscopic properties of both monolayer assemblies and electrodeposited films of these polymers.

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